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Test Methods for Determining Free Acid and Free Alkali in Greases

Report by Mr. Gus Kaufman, Chairman of Sub-Committee on Free Acid and Free Alkali
National Lubricating Grease Institute

Introduction

The personnel of the Sub-Committee on Free Acid and Free Alkali, and the participating companies, are as follows:

Battenfeld Grease and Oil Corp.
Mr. R. R. Matthews
Socony Vacuum Oil Co.
Mr. T. G. Roehner
Standard Oil Development Co.
Dr. J. C. Zimmer
The Texas Company
Mr. Gus Kaufman, Mr. R. S. Barnett
Union Oil Company
Mr. T. F. Ott, Mr. L. W. McLennan

The work discussed in this report covers the following scope:

1. Test Methods
   a. Short-comings of present ASTM Method D 128-40
   b. Recommendations for a more suitable method for alkali metal and alkaline earth metal greases
2. Free acidity in greases made from weak bases
3. Practical significance of alkalinity and acidity

TEST METHODS

1. Statement of the Problem

As alkali metal (sodium, potassium, lithium) and alkaline earth metal (calcium, barium) greases comprise the volume of commercial products sold today, this report will deal mainly with the determination of free acid and free alkali in such greases. A brief section is included to present the status of the determination of free acidity in greases made from weak or insoluble bases which are unsuitable for straightforward acidimetric and alkalimetric titration methods. Such products are those containing the soaps of aluminum, lead, zinc, magnesium, etc., as well as organic bases such as triethanolamine, to be discussed later.

2. Short-comings of Present ASTM Method D 128-40

a. Objectives for a Satisfactory Method

(1) Co-existence of Free Acids and Free Alkali in Greases

The co-existence of free acid and free alkali in lubricating greases has apparently been well established as discussed in the following paragraphs. Such co-existence depends on a definition of free alkali as including carbonates and alkaline earth metal hydroxides but excluding alkali metal hydroxides; in other words, free acidity has not been found in the presence of free caustic hydroxides.

The simultaneous presence of sodium carbonate and free fatty acids in soap has been recognized by The Analytical Methods Committee of the Society of Public Analysts[1]. Furthermore E. R. Luckow[2] has shown that the presence of dissolved sodium soap lessens the interaction between free sodium carbonate and free oleic acid in strong alcohol.

The foregoing co-existence of free acid and free alkali in soaps has been confirmed for lubricating greases by the work of Levin, Barnett and McDowell of The Texas Company[3] as shown by the following tabulated data on known mixtures. Table I, page 4, indicates that oleic acid may be successfully determined in calcium soap cup grease in the presence of a large amount (4.0%) of added calcium hydroxide. Table II, page 5, presents data to show that oleic acid may be successfully determined in the presence of a large excess (10.0%) of added sodium carbonate in a sodium soap sponge grease. Table III, page 6, indicates that varying amounts of added oleic acid may be determined with satisfactory accuracy when added to a mixed base (sodium-calcium) grease containing 0.6% free sodium carbonate.

(2) Important Constituents

The complete analytical examination of grease for free acid and free alkali may be a quite complex and tedious procedure; for instance, take the case of a sodium-calcium grease which may have become badly oxidized after long storage under catalyzing conditions. The following tests would be needed to give an over-all picture of the type and kinds of free acid and free alkali existing in such a sample.

FREE ACID

1. Non-volatile and/or non-water-soluble (usually non-corrosive)
2. Volatile and/or water-soluble (usually corrosive)

FREE ALKALI

1. Carbonates (sodium, calcium)
2. Calcium hydroxide

While an extended analysis, including extraction, centrifuging and distillation procedures probably could be worked out to determine the above constituents it does not seem feasible or necessary to have such involved methods for an inter-organizational standard method. For instance, the presence of corrosive free acidity can be determined by suitable steel and/or copper corrosion tests without the necessity for an involved quantitative determination of the acids in question.

Total free alkali expressed as carbonate would seem to satisfactorily express the alkalinity of commercial greases, as initial free

hydroxide changes over to carbonate on storage or service. It has been the experience of The Texas Company, based on the examination of a great many grease samples, that commercial sodium base greases rarely contain free NaOH, and that freshly-made sodium soap grease tends to lose any alkali hydroxide alkalinity on storage and/or use, with carbonate being formed as the end-product. Therefore, a quantitative distinction between free hydroxide and free carbonate, though desirable from a research standpoint, is probably not too important from a practical or service standpoint. In addition, methods using substantially anhydrous solvents qualitatively distinguish between free alkali hydroxide and carbonates by showing an alkaline reaction to phenolphthalein in the initial disintegration of the grease by the solvents in question when free caustic is present.

The following definitions of free acid and free alkali are therefore presented as capable of satisfactory determination for a standard method.

1. Total free fatty acid as oleic.
2. Total free alkali as carbonate of predominating base.

b. Comparison of ASTM Methods D 128-27 and D 128-40

Table IV, facing presents a comparison of the old ASTM Method D 128-27 (E) versus the present ASTM Method D 128-40 (18,19,20) as regards solvents, size of sample, indicator, procedure, and limitations. The ASTM Methods, at maximum effectiveness, determine only the excess of one constituent over the other. D 128-27 was in force until 1937 when the free acidity method was revised by changing the ethyl alcohol strength from 50% to 95%.

The use of diluted (50%) alcohol introduces the following further inaccuracies in D128-27.

1. Incomplete disintegration of calcium soap and sodium-calcium soap greases.
2. Evidence exists that the apparent alkalinity of certain commercial sodium base greases is due largely to the hydrolysis of certain soaps (such as sodium naphthenate) in the diluted alcohol.
3. Certain sodium soap greases introduce a deep red-brown color in the aqueous layer which makes it practically impossible to decide whether they are acid or alkaline to phenolphthalein, and also obscure the acidity end-point in any case.

The use of 95% alcohol induces the following further inaccuracies in D 128-40.

1. Sodium soap greases containing sodium carbonate, which had been found alkaline by D 128-27, were found acid by D 128-40, thus precluding any determination of free alkali by ASTM D 128-40 as this method is set up so that greases showing an initially acid reaction are not analyzed for free alkali. This short-coming of the ASTM method has also been commented on by Roehner[4] of Socony Vacuum Oil Company.

Product	*Type of Soap*	*ASTM Method D 128-27, %*	*ASTM Method D 128-40, %*
High Heat Grease	Sodium	0.20 as NaOH	0.28 as oleic acid
High Heat Grease	Sodium	0.20 as NaOH	0.28 as oleic acid
Sponge Grease	Sodium	0.03 as NaOH	0.14 as oleic acid
Experimental Grease	Sodium	0.05 as NaOH	0.05 as oleic acid
Cup Grease	Calcium	0.11 as $Ca(OH)_2$	0.11 as $Ca(OH)_2$
Ball & Roller Bearing Grease	Sodium, Calcium	0.11 as NaOH	0.04 as NaOH
Ball & Roller Bearing Grease	Sodium, Calcium	0.19 as NaOH	0.10 as NaOH

The following tabulation presents data on this point[5].

The foregoing results indicate that carbonate is entirely missed in the D 128-40 method unless calcium hydroxide is simultaneously present, as $Ca(OH)_2$ is apparently soluble enough in 95% alcohol to give an alkaline reaction and so permit of proceeding to the free alkali determination of D 128-40. In the last two tests, the higher results for free alkali obtained by D 128-27 are due probably to a premature end-point caused by hydrolysis of sodium soap in the dilute alcohol of D 128-27.

Both the present and superseded ASTM methods use petroleum naphtha as one of the solvents, which introduces a fire hazard as stressed by Matthews of Battenfeld[6]. When the samples are refluxed with standard acid in the free alkali determination and then removed hot for immediate titration, fumes of naphtha escape into the air in appreciable quantities.

c. Improved Methods for Free Alkali and Free Acid

(1) Refluxing Initially all Samples with Standard Acid, and Back-titrating with Standard Base

This method improves ASTM D 128-40 by giving a better end-point for dark greases, and by including carbonates in every case. If the back titration goes over the blank, then the sample contains an excess of acidity over free alkalinity. In this case the net titre is calculated as oleic acid.

Zimmer[7] has reported that method (1) is used by the Standard Oil Development Company, with The Texas Company[8] also using it. The latter organization utilizes this method only when mandatory to follow the ASTM procedure as closely as possible on dark greases.

The foregoing method, however, still determines only the excess of one constituent over the other and so does not portray the conditions usually existing in lubricating greases; that is, the co-existence of free alkali and free acid, which may have definite practical significance as brought out subsequently.

(2) Electrometric Titration

ASTM Designation D 664-42T covers a tentative electrometric titration method for petroleum products, including modern inhibitor and detergent-containing oils. It is stated as applicable to those substances showing complete or nearly complete solubility in benzene-isopropyl alcohol mixtures. Because of this fact it is considered generally unsuitable for greases as the insolubility of carbonates in organic solvents would preclude their determination by this method.

(3) Determination of Co-existing Free Acid and Free Alkali by Direct Titration of Acidity Followed by Refluxing with Standard Acid and Back-titrating with Standard Base

This is The Texas Company method as developed at its Beacon Research Laboratory[8]. This method has had wide application over a number of years to a great many grease samples, and has proved a valuable and accurate tool both for research and technical service evaluations.

The Texas Company method uses a solvent mixture of equal parts of benzene and substantially anhydrous isopropyl alcohol. This solvent mixture permits of the determination of free acid in the presence of co-existent free alkali as heretofore defined. It is quite probable that free acid is practically non-existent in a grease containing excess free *alkali hydroxide*, though no method is known of proving this point as solvent disintegration of such a grease would permit of the neutralization of any free acid by free alkali hydroxide, both constituents being soluble in oxygenated solvents.

The Texas Company method has been found valid for all alkali metal and alkaline earth metal greases tested (including lithium greases) with the possible exception of barium grease containing basic soap, in which there is some evidence that such basic soap may be destroyed wholly or partially by refluxing with standard acid, the consumed acid being included in the titration difference and necessarily calculated as free alkali.

Data in the foregoing Tables, I, II and III have demonstrated that The

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Texas Company method determines free acid in the presence of large amounts of free alkali carbonate (Na_2CO_3) and alkaline earth hydroxide [$Ca(OH)_2$]. Table V, page 14, shows that either hot or cold disintegration may be used to determine free acidity in calcium soap grease, the hot disintegration being, of course, more rapid. It is perhaps more accurate, however, to use cold disintegration (room temperature) whenever possible, because lower free fatty acids of greater reactivity may be present in oxidized samples, and boiling up with solvents may accelerate interaction with any free alkali simultaneously present.

Tables VI, VII and VIII, pages 15, 16, and 17, demonstrate the accuracy which may be expected in determination of both free alkalinity and free acidity added in varying amounts to the same base greases. The results are shown for a series of knowns prepared by adding both alkali [$Ca(OH)_2$ and $CaCO_3$] and free oleic acid to a calcium soap cup grease, and Na_2CO_3 to a sodium soap sponge grease. In each of these tests the disintegration of the grease for determination of acidity was done by refluxing with the solvent for two minutes. The accuracy of this method on known mixtures, though not particularly impressive, is within the experimental error commonly experienced in grease analysis titrations, and, of course, portrays a much more complete picture of free acid and free alkali than the ASTM methods or modifications of them. The exact titrations possible in the analysis of detergent soaps are not so easily achieved with lubricating greases.

The foregoing Texas Company method has been circularized to members of Sub-Committee IV, ASTM Committee D-2, and the Sub-Committee has voted favorably on this method after considering reports from participating laboratories who had tried it out independently. Sub-Committee IV has decided to carry out cooperative work on standard samples to establish inter-laboratory reproducibility, etc.

The following sections explain and give in detail the two steps of the Texas Company method.

Part A of the method consists of the direct titration of free acidity with 0.1N alcoholic potassium hydroxide to phenolphthalein, having disintegrated the sample with a solvent mixture of benzene and isopropyl alcohol (98%—may contain up to 2% water).

The use of small samples when necessary insures rapid disintegration, clearer end-points for dark greases, and economy of sample when only small amounts are available as from stored or used bearings. The use of 0.1 N solution helps to maintain the sensitivity of the method. Benzene is more efficient in disintegrating greases than solvents such as petroleum ether and is less of a fire hazard, while the use of substantially anhydrous alcohol minimizes the tendency for interaction of sodium carbonate and free fatty acid when both are present in a grease; similarly for calcium hydroxide and free fatty acid present in a grease.

Part B of the method consists of adding an excess of 0.5 N aqueous hydrochloric acid to the neutralized solution resulting from Part A, refluxing, then titrating the excess of acid with 0.5 N alcoholic potassium hydroxide to phenolphthalein, having added pure isopropyl alcohol just prior to making the titration to secure a one phase medium.

Aqueous hydrochloric acid is used to insure complete reaction of the entire free alkali, and the amount of 0.5 N acid must be more than sufficient to react with the soap, in order to insure complete reaction of the free alkali.

The free alkali is calculated in terms of the carbonate in the case of soda base greases, because of the rarity of the presence of free sodium hydroxide in the commercial kettle-made products when they reach the laboratory for test; likewise to the carbonate in the case of lime base cup greases.

The method in detail is now given below:

DETERMINATION OF FREE ALKALI AND FREE ACID CO-EXISTING IN GREASE

Part A—Determination of Free Acid

A 2-10 gram sample of the grease shall be weighed in a 250 ml. Erlenmeyer flask, smearing the grease along the inside of the flask with a glass rod to facilitate disintegration. To this shall be added 100 ml. of a neutral mixture of equal volumes of benzene and 98% isopropyl alcohol, and some

(Continued on page 6)

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TABLE I

DETERMINATION OF FREE FATTY ACID CO-EXISTING WITH FREE ALKALI IN A CALCIUM CUP GREASE

Product	*$Ca(OH)_2$ per cent added*	*Oleic acid, per cent added*	*Oleic acid, per cent present (1)*	*Oleic acid, per cent found (1)*
Cup Grease #3	None	None		1.0
Cup Grease #3	4.0	5.7	6.7	6.8
Cup Grease #3	4.0	5.8	6.8	6.8
Cup Grease #3	4.0	5.7	6.7	6.7

(1) This is the sum of that added and that found in the original grease by the authors' method.

(2) In this series of tests the grease was disintegrated by refluxing with the solvent for ten minutes.

TABLE II

DETERMINATION OF FREE FATTY ACID CO-EXISTING WITH FREE ALKALI IN A SODIUM SPONGE GREASE

Product	*Na_2CO_3 per cent added*	*Oleic acid, per cent added*	*Oleic acid, per cent present (2)*	*Oleic acid, per cent found (1)*	*Free Alkali per cent found in terms of Na_2CO_3*
Sponge Grease	None	None	....	0.1	None
Sponge Grease	10.0	5.8	5.9	6.0	....
Sponge Grease	10.0	5.7	5.8	5.6	....

(1) This is the sum of that added and that found in the original grease by the authors' method.

(2) In this series of tests the grease was disintegrated by refluxing with the solvent for ten minutes.

TABLE III

DETERMINATION OF FREE FATTY ACID CO-EXISTING WITH FREE ALKALI IN A MIXED BASE (SODIUM-CALCIUM) BALL-BEARING GREASE

Product	*Oleic acid, per cent added*	*Oleic acid, per cent present (2)*	*Oleic acid, per cent found(1)*	*Free Alkali per cent found in terms of Na_2CO_3*
Ball-bearing grease	None	....	0.1	0.6
Ball-bearing grease	6.0	6.1	6.2	....
Ball-bearing grease	5.1	5.2	5.2	....
Ball-bearing grease	7.6	7.7	7.7	....
Ball-bearing grease	13.8	13.9	14.2	....
Ball-bearing grease	13.9	14.0	14.1	....

(1) This is the sum of that added and that found in the original grease by the authors' method.

(2) In this series of tests the grease was disintegrated by digesting with the solvent at room temperature.

TABLE IV

COMPARISON OF THE FORMER AND PRESENT ASTM METHODS

Requirement	*Old ASTM, D 128-27 (E)*	*Present ASTM D 128-40 (18, 19, 20) (Free Acid Determination Revised in 1937)*
Size of Sample, grams	10-30	10-30
Solvent Mixture	75 ml. petroleum ether 50 ml. 50% alcohol	75 ml. petroleum ether 50 ml. 95% alcohol
Indicator	Phenolphthalein	Phenolphthalein
Disintegration	In cold	In cold
Determination of Free Acidity	If the alcoholic layer is not pink, titrate acidity in cold with 0.5N alcoholic KOH.	
Determination of Free Alkali	If the alcoholic layer is pink, add 10 ml. of 0.5 N HCl, reflux for 10 minutes, back titrate with 0.5N alcoholic KOH	
Limitations	At maximum effectiveness determines only the excess of one constituent over the other.	Misses free alkali entirely in most sodium base greases, as Na_2CO_3 insoluble in 95% alcohol. At maximum effectiveness, determines only the excess of one constituent over the other.

TABLE V

COMPARISON OF THE EFFECTS OF HOT AND COLD METHODS OF DISINTEGRATION, ON THE RESULTS OBTAINED FOR ACIDITY ON A COMMERCIAL LIME CUP GREASE

	Acidity as oleic acid — per cent			
Cold agitating period	*Test 1*	*Test 2*	*Test 3*	*Test 4*
30 minutes	0.6	0.7	0.8	....
60 minutes	0.9	0.9	0.9	....
90 minutes	1.0	1.0	1.1	....
120 minutes	1.0	1.0	1.1	....
Refluxing for ten minutes	1.0	1.1	1.1	1.0
Refluxing for thirty minutes	1.1	1.2	....	....

TABLE VI

FREE ACID AND FREE CALCIUM HYDROXIDE SIMULTANEOUSLY PRESENT IN KNOWN AMOUNTS IN CUP GREASE

Product	*Free $Ca(OH)_2$*		*Free Oleic Acid**	
Calcium Soap Cup Grease No. 3	*Present(1)*	*Found*	*Present(1)*	*Found*
Test No.				
Original Grease	....	0.17**	....	0.9**
1	0.36	0.33	2.8	2.6
2	1.15	1.09	10.1	9.6

(1) Sum of amount found in original grease plus added increment.
* Samples boiled with the solvents for two minutes prior to titration.
** Titre calculated to pertinent constituent.

TABLE VII

FREE ACID AND FREE CALCIUM CARBONATE SIMULTANEOUSLY PRESENT IN KNOWN AMOUNTS IN CUP GREASE

Product	*Free $CaCO_3$*		*Free Oleic Acid**	
Calcium Soap Cup Grease No. 3	*Present(1)*	*Found*	*Present(1)*	*Found*
Test No.				
Original Grease	....	0.22**	....	0.9**
1	0.42	0.41	2.8	2.7
2	1.22	1.18	10.1	9.6

(1) Sum of amounts found in original grease plus added increment.
* Samples boiled with the solvents for two minutes prior to titration.
** Titre calculated to pertinent constituent.

TABLE VIII

FREE ACIDS AND SODIUM CARBONATE SIMULTANEOUSLY PRESENT IN KNOWN AMONTS IN SPONGE GREASE

Product	*Free Na_2CO_3*		*Free Oleic Acid**	
Sodium Soap Sponge Grease	*Present(1)*	*Found*	*Present(1)*	*Found*
Test No.				
Original Grease	....	None	....	0.1**
1	0.20	0.17	1.0	0.9
2	0.99	0.95	4.7	4.6

(1) Sum of amount found in original grease plus added increment.
* Samples boiled with the solvents for two minutes prior to titration.
** Titre calculated to oleic acid.

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Test Methods for Determining Free Acid and Free Alkali in Greases

(Continued from page 3)

glass beads to further facilitate disintegration. The grease shall be disintegrated by agitation, or by heating under a reflux condenser if necessary, and the free acid promptly titrated with 0.1 N alcoholic potassium hydroxide, using phenolphthalein as indicator. The free acid shall be calculated in terms of oleic.

NOTE:—It is preferable to effect the disintegration of the grease at room temperature whenever possible because lower free fatty acids of greater reactivity may be present and the higher temperature may accelerate their interaction with free alkali simultaneously present. Refluxing with these solvents did not cause a material combination of free calcium hydroxide with free fatty acid, nor of free sodium carbonate with free fatty acid, when these were present in experimental greases to which the method was applied. It was also noted in the tests on these experimental greases that the presence of increasing amounts of free fatty acids caused the grease to disintegrate more readily in the test. Some greases are particularly difficult to disintegrate and on such it has been found helpful to add the benzene component alone, reflux for a few minutes and then add the isopropyl alcohol component and continue in the usual manner. In the rare case of an initially alkaline reaction, proceed directly to Part B — Determination of Free Alkali.

Part B—Determination of Free Alkali

To the neutralized solution remaining after the determination of free acid (or to the original solution if initially alkaline) shall be added 20 ml. of 0.5 N aqueous hydrochloric acid and the mixture boiled under a reflux condenser for 10 minutes. 50 ml. of neutral 98% isopropyl alcohol shall then be added and the excess of acid promptly titrated with 0.5 N alcoholic potassium hydroxide to phenolphthalein as indicator. The free alkali shall be calculated in terms of the carbonate of the predominating base.

3. Free Acidity in Weak or Insoluble Base Greases

None of the methods discussed in the foregoing are suitable for the determination of free acidity or free "alkalinity" in greases made from amphoteric metals such as Al, Zn, Pb, Sn, etc. This is, of course, because the metals are displaced by the strong base of the usual alkalimetric procedure, forming oxides and/or hydroxides which are too insoluble to react alkaline to phenolphthalein and which redissolve in an excess of caustic. Magnesium, while not amphoteric, is displaced by potash to give an alcohol-insoluble base which will not redden phenolphthalein. Organic bases such as triethanolamine are also too weak in alcohol to affect phenolphthalein, an indicator of this type being necessary for the alkalimetric titration of higher fatty acids.*

Much work has been done by various laboratories in an effort to find a satisfactory method for the foregoing determination but to date no completely satisfactory and accepted procedure has been developed. The picture is complicated by the varying degrees of hydrolysis of soaps of weak bases, so that it has been difficult to find one generally applicable method.

Methods for solvent extraction of the free fatty acids, such as reported by McLennan[8] as used by the Union Oil Company for aluminum base grease are indicated to be fairly successful, though complicated by the presence of dissolved soaps in the solvent extracts. Levin and coworkers[9], The Texas Company have had success with a method applicable to powdered soaps of weak bases, such as aluminum stearate, which is substantially a refinement of the Union Oil Company acetone extraction method though developed independently. In Levin's method, several samples varying in weight by a constant factor (1, 3 and 5 g. for instance) are refluxed with equal volumes of acetone and aliquots of the extracts titrated. It is assumed that each extract is saturated with respect to dissolved soap, therefore, the titre for the 3 g. sample minus the titre for the 1 g. sample would be equivalent to the free acid content in a 2 g. sample, thus correcting for the presence of dissolved soap. Likewise 5 g. titre—1 g. titre is equivalent to FFA in 4 g. sample.

As regards free "alkalinity" in greases made from the soaps of weak bases, this is not considered a significant problem. Because of their insolubility, the oxides, carbonates and hydroxides of weak bases are commonly not considered alkaline in the usual sense. In addition, their presence and extent may be ascertained by determination as insoluble residues by usual solvent extraction methods.

It is recommended that the National Lubricating Grease Institute appoint a committee to give further study to the problem of free acidity in greases made from weak soap bases. It is suggested that the acetone extraction method, as developed by the Union Oil Company and The Texas Company, be studied first because of the promising results obtained so far, and because of its simplicity as compared to electrometric methods, for instance.

*Total triethanolamine can be titrated to methyl orange in an alcoholic solution of triethanolamine soap, if desired.

PRACTICAL SIGNIFICANCE

1. Importance of an Accurate Method for Free Acid and Free Alkali

An accurate estimation of co-existent free alkali and free acid is a significant aid in the control of manufacture of lubricating greases, allowing the manufacturer to

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limit these constituents to desired ranges which are important in certain cases for the establishment of desired grease structures, melting point ranges, and the like. With such a method, the rate of saponification of products such as cold set greases made from organic acids and strong bases can be followed.

The accurate determination of free acid and free alkali is also important in analysis of used or deliberately-oxidized greases. For instance, it has been found that the high temperature decomposition of a sodium soap grease under heavy service may result in the build-up of co-existent free carbonate and free acidity in amounts of ½ per cent. The analysis of high free alkali greases after the Norma-Hoffmann Oxidation Test affords an example of how increase in free acidity may be checked against changes in the free alkali content of the grease if desired.

2. Influence of Free Alkali on the Characteristics of Grease

Because of the variety and complexity of present day grease formulas it is difficult to make a valid generalization as to the effect of free alkali. It is the Sub-Committee's feeling that arbitrary specifications on such constituents be discouraged, and that greases be evaluated by practical tests as far as possible. Further work should be done on the possible abrasion characteristics of large amounts of free alkali.

3. Influence of Free Acidity on the Characteristics of Grease

Here again it is difficult to generalize on the effect of free acidity on the performance properties of greases. For instance, greases on long time service may develop as much as five per cent free fatty acids as oleic without causing bearing corrosion or unsatisfactory lubrication. Amount of free acid of the order of one per cent are commonly found in present day lithium base greases without apparent harm to bearings.

As brought out in the discussion of free alkali it is recommended that the National Lubricating Grease Institute seek to educate the public to judge greases by performance tests rather than by composition specifications; in other words, free alkali and free acid should be considered not as harmful impurities but as controlled additives incorporated to improve performance in many cases.

CONCLUSIONS

The following conclusions are drawn, based on the foregoing.

1. Proof has been offered of the co-existence of free fatty acid and free alkali (excluding alkali hydroxides) in lubricating grease.

2. A method has been proposed which determines co-existent free acid and free alkali with apparently satisfactory accuracy, and which is much more accurate than either ASTM D 128-27 or D 128-40, both of which measure at maximum effectiveness only the excess of one constituent over the other.

3. No completely satisfactory or generally accepted procedure for determining free acidity in greases made from the soaps of weak bases has been developed. The acetone extraction method, corrected for dissolved soap, appears to be the most promising.

4. An accurate method for determining free acid and free alkali is important in manufacturing control, rate of saponification studies, etc., and has useful applications in the analysis of used or deliberately-oxidized greases. As definite amounts of free acid and/or free alkali may improve the performance characteristics of greases and be important for proper structure, these constituents should not be considered as impurities by purchasers, but as closely controlled additives.

RECOMMENDATIONS

The following recommendations are made:

1. That the method for the determination of free acid and free alkali co-existing in lubricating grease, as described on pages 20 and 21 of this report, be investigated for suitability as a standard method for free acid and free alkali in alkali metal and alkaline earth metal greases.

2. That the committee on Free Acid and Free Alkali in Greases be continued to study the determination of free acidity in greases containing soaps of weak bases, first considering the acetone extraction method developed by the Union Oil Company and The Texas Company; and that this committee also study the possible abrasive effects to bearings of large amounts of free alkali.

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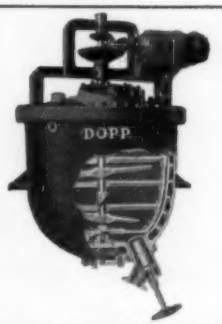

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